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<p>(21) International Application Number: PCT/GB97/02380</p> <p>(22) International Filing Date: 4 September 1997 (04.09.97)</p> <p>(30) Priority Data:</p> <table border="0"><tr><td>9618474.2</td><td>4 September 1996 (04.09.96)</td><td>GB</td></tr><tr><td>9618473.4</td><td>4 September 1996 (04.09.96)</td><td>GB</td></tr><tr><td>9618475.9</td><td>4 September 1996 (04.09.96)</td><td>GB</td></tr></table> <p>(71) Applicant (for all designated States except US): CAMBRIDGE DISPLAY TECHNOLOGY LIMITED [GB/GB]; 13 Station Road, Cambridge CB3 0DJ (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): PICHLER, Karl [AT/GB]; 3 Victoria Park, Cambridge CB4 3EJ (GB).</p> <p>(74) Agents: DRIVER, Virginia, Rozanne et al.; Page White & Farrer, 54 Doughty Street, London WC1N 2LS (GB).</p>		9618474.2	4 September 1996 (04.09.96)	GB	9618473.4	4 September 1996 (04.09.96)	GB	9618475.9	4 September 1996 (04.09.96)	GB	<p>(81) Designated States: CN, GB, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>
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<p>(54) Title: ORGANIC LIGHT-EMITTING DEVICES WITH IMPROVED CATHODE</p> <div data-bbox="410 1422 1786 1799"></div> <p>(57) Abstract</p> <p>An organic light-emitting device wherein the cathode (4, 5) comprises a first layer (5) of a conducting material and a second layer (4) of a conductive material having a work function of at most 3,7 eV and wherein the second layer is substantially thinner than the first layer, having a thickness of at most 5 nm.</p>											

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ORGANIC LIGHT-EMITTING DEVICES WITH IMPROVED CATHODE

The field of the invention relates to organic light-emitting devices with efficient electron injecting electrodes.

Organic light-emitting devices (OLEDs) such as described in earlier US patent No. 5,247,190 assigned to Cambridge Display Technology Limited, or in Van Slyke et al., US No. 4,539,507, the contents of which are herein incorporated by reference and example, have great potential for use in various display applications. Principally, an OLED consists of an anode that injects positive charge carriers, a cathode that injects negative charge carriers and at least one organic electroluminescent layer sandwiched between the two electrodes. One of the key advantages of the OLED technology is that devices can be operated at low drive voltages, provided that suitable electro-luminescent organic layers, and electrodes with good efficiencies for the injection of positive and negative charge carriers, are used. Typically although not necessarily the anode is a thin film of, for example, indium-tin-oxide (ITO), which is a semi-transparent conductive oxide which is commercially readily available already deposited on glass or plastic substrates. The organic layer(s) is normally deposited onto the ITO-coated substrate by, for example, evaporation, or any one of spin-coating, blade-coating, dip-coating or meniscus-coating. The final step of depositing the cathode layer onto the top organic layer is normally performed by thermal evaporation or sputtering of a suitable cathode metal. Layers of Al, Ca or alloys of Mg:Ag or Mg:In or Al alloys are often used as cathode materials. In order to achieve good performance in OLEDs it is of great importance to optimise all individual layers, the anode, the cathode and the organic layer(s), as well as the interfaces between the layers.

It is very often found that the electron-injection properties of the cathode are particularly important to achieve efficient device operation. Due to the electronic structure of most organic electroluminescent materials it is very often necessary

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to employ cathode materials with a low work function to achieve efficient electron injection and low operating voltages. Such cathodes for OLEDs are typically alkali metals such as Li, Na, K, Rb or Cs, alkaline earth metals such as Mg, Ca, Sr or Ba or lanthanides such as Sm, Eu, Tb or Yb. These materials tend to react very readily with oxygen and moisture and particular care has to be taken on handling and/or during and after deposition onto OLEDs. Often these low work function materials are deposited as cathode layers onto OLEDs in the form of alloys whereby other alloy constituents stabilise the cathode layer; typical such alloys are for example Mg:Al, Mg:In or Mg:Ag or Al:Li. When using some of these low work function elements, for instance Ca, K, Li or Sm in pure or alloy form as OLED cathode layers these elements can diffuse into the organic layer(s) and subsequently dope the organic layer(s), cause electrical shorts or quench photo-luminescence, and therefore generally deteriorate device performance.

It is thus an object of the present invention to provide a structure, and method of fabrication for, an organic light-emitting device that incorporates low work function elements as cathodes to achieve efficient injection of negative charge carriers and low operating voltage, but minimises at least some of the problems outlined above.

According to a first aspect of the present invention there is provided an organic light-emitting device, comprising at least one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is an opaque metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material, having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic

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compound having a work function of at most 3.7 eV.

Thus, the cathode is composed of a thin layer of an elemental metal, alloy or inter-metallic compound, with a work function of at most 3.7 eV, but preferably less than 3.2 eV. The cathode layer has a thickness of at most 5 nm, but preferably of between 0.5 and 2 nm thick. The thin, low work function cathode layer is preferably capped with another conductive layer, typically 100 - 500 nm thick, which provides high conductivity protection for the underlying thin, low work function layer, as well as environmental stability. Such a bi-layer electrode structure according to the first aspect of the present invention forms a cathode layer with efficient electron injection for an OLED with at least one electro-luminescent organic layer between said cathode layer and an anode layer, the anode layer for injecting positive charge carriers.

Such a structure prevents excessive doping and minimises the risk of shorting of the device structure and quenching of the electro-luminescence of the at least one layer of organic material.

The first aspect of the invention also provides a method of fabricating an organic light-emitting device, comprising the steps of forming a cathode for the device over a substrate, which step comprises forming a first layer of a conductive material of high conductivity over a substrate and forming a second layer of a conductive material having a low work function over the first layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV, forming at least one layer of a light-emissive organic material over the cathode and forming an anode for the device over the at least one layer of organic material.

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The first aspect of the invention further provides a method of fabricating an organic light-emitting device, comprising the steps of forming an anode for the device over a substrate, forming at least one layer of a light-emissive material over the anode and forming a cathode for the device over the at least one layer of organic material, which step comprises forming a second layer of a conductive material having a low work function over the at least one layer of organic material and forming a first layer of a conductive material of high conductivity over the second layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV.

Thus there is also provided a method of fabrication for an OLED with an efficient electron-injecting electrode in which at least one electro-luminescent organic layer, preferably either polymeric or molecular, is deposited preferably onto a supportive substrate pre-coated with an anode. The organic layer is coated in one embodiment by vacuum evaporation, with a thin layer of conductive, low work function material. This layer is at most 5 nm but preferably between 0.5 and 2 nm thick, and still more preferably about 0.5 nm. This thin layer is typically, but not essentially, an alkali metal, alkaline earth metal or a lanthanide or an alloy or inter-metallic compound incorporating one or more of said alkali metal, alkaline earth metal or lanthanide elements. The thin low work function layer is then preferably covered with a thick conductive layer of typically 100 to 500 nm thickness which provides high conductivity, protection for the underlying thin low work function layer and environmental stability, and which is preferably applied by vacuum evaporation or sputter deposition.

According to a second aspect of the present invention there is provided an organic light-emitting device, comprising at least

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one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is a DC magnetron sputtered metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material.

Such a structure provides advantages similar to those discussed above with reference to the first aspect of the present invention.

The invention will now be described with reference to a particular example as shown in the accompanying drawing, in which:

Figure 1 illustrates a structure of an OLED in accordance with the present invention.

According to the illustrated embodiment of the invention, an OLED is formed by first forming a semi-transparent anode deposited onto a transparent supportive substrate. The substrate is, for example, a thin sheet of glass or plastic such as polyester, polycarbonate, polyimide, poly-ether-imide or the like. Referring to Figure 1, a glass substrate 1 is covered with a layer of a semi-transparent conductive indium-tin-oxide (ITO) layer 2, typically about 150 nm thick with a sheet resistance of typically ≤ 30 Ohms/square. Although the semi-transparent anode shown in Figure 1 is a thin layer of conductive oxide such as indium-tin-oxide, it may alternatively be a doped tin-oxide or zinc-oxide.

The organic layer(s) deposited on top of the anode/substrate is/are preferably, but not necessarily, one or more layers of an electro-luminescent conjugated polymer such as described in

earlier US No. 5,247,190 assigned to Cambridge Display Technology Limited. Such organic layer is formed to a thickness typically of the order of 100 nm thick. Alternatively the organic layer(s) could be low molecular weight compounds such as described in US patent No. 4,539,507, or a combination of layer(s) of conjugated polymer(s) with layer(s) of low molecular weight compound(s). In Figure 1, the ITO layer is covered with a ca. 100 nm thick layer 3 of the electroluminescent polymer poly(p-phenylene vinylene), PPV, as for example described in US patent No. 5,247,190.

The cathode may be a thin layer of an alkali metal, alkaline earth metal or a lanthanide or an alloy or inter-metallic compound incorporating one or more of said alkali metal, alkaline earth metal or lanthanide elements. The cathode layer is at most 5 nm but preferably between 0.5 and 2 nm thick and examples for materials which may be used are Li, K, Sm, Ca or an Al:Li alloy. In the example of Figure 1, the PPV layer 3 is preferably covered with a 0.5 nm thick layer 4 of Li deposited by vacuum sublimation of the Li from a commercial Al:Li alloy.

The thin layer of the cathode may be sputter deposited, preferably by DC magnetron sputtering or RF sputtering. The thin layer of the cathode may also be evaporated, preferably by resistive evaporation or electron beam thermal evaporation.

The thin layer of the cathode, being a conductive material comprising either an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV, and preferably at most 3.2 eV.

The thin layer is then preferably covered with a conductive layer of, for example, aluminium or an aluminium alloy which is typically between 100 and 500 nm thick, and preferably about 100 nm. In Figure 1, the thin layer 4 is, without breaking vacuum, preferably covered with a 150 nm thick layer 5 of Aluminium deposited by vacuum evaporation.

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The thick conductive layer may be sputtered, preferably by DC magnetron sputtering or RF sputtering. The thick layer may also be evaporated by resistive evaporation or electron-beam thermal evaporation.

Preferably, the ratio of the thickness of the thick conductive layer to the thin layer is 20:1.

The layer thicknesses are controlled by a standard quartz crystal thickness monitor in combination with a shutter.

In an alternative arrangement, the two-layer cathode described with reference to Figure 1 is formed on the substrate, the at least one layer of a light-emissive organic material is formed over the cathode, and the anode formed over the at least one layer of light-emissive organic material.

The thin layer of Li provides excellent electron injection and low turn-on and operating voltage and, although diffusion of the Li from layer 4 into the PPV layer 3 with subsequent doping and quenching of electro-luminescence in the PPV is not prohibited, the limited thickness and hence amount of material of layer 4 prevents excessive doping and electro-luminescence quenching.

There thus has been described a device structure, and process of fabrication thereof, for an OLED with an efficient low work function electron-injecting cathode with minimised risk of excessive doping of the organic layer(s) by the low work function cathode, and therefore minimised risk of shorting of the device structure and quenching of electro-luminescence.

Claims:

1. An organic light-emitting device, comprising at least one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is an opaque metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material, having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV.
2. An organic light-emitting device according to claim 1, wherein the second layer of conductive material has a thickness in the range of from 0.5 to 2 nm.
3. An organic light-emitting device according to claim 1 or claim 2, wherein the second layer of conductive material has a thickness of about 0.5 nm.
4. An organic light-emitting device according to any one of claims 1 to 3, wherein the first layer of conductive material has a thickness in the range of from 100 to 500 nm.
5. An organic light-emitting device according to claim 4, wherein the first layer of conductive material has a thickness of about 150 nm.
6. An organic light-emitting device according to any of claims 1 to 5, wherein the first layer of conductive material comprises Al or an alloy thereof.
7. An organic light-emitting device according to any of claims 1 to 7, wherein the second layer of conductive material comprises

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an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.2 eV.

8. An organic light-emitting device according to any of claims 1 to 7, wherein the second layer of conductive material comprises one of an alkali metal, an alkaline earth metal or a lanthanide, or an alloy or an intermetallic compound thereof.

9. An organic light-emitting device according to claim 8, wherein the second layer of conductive material comprises one of Ca, K, Li, Sm or an Al-Li alloy.

10. An organic light-emitting device according to any of claims 1 to 9, wherein the ratio of thicknesses of the first layer of conductive material to the second layer of conductive material is at least 20 : 1.

11. An organic light-emitting device according to any of claims 1 to 10, wherein the at least one layer of organic material has a thickness of about 100 nm.

12. An organic light-emitting device according to any of claims 1 to 11, wherein the organic material is a conjugated polymer.

13. An organic light-emitting device according to any of claims 1 to 11, wherein the organic material is a low molecular weight compound.

14. An organic light-emitting device according to any of claims 1 to 11, wherein the at least one layer of organic material comprises a composite structure including at least one layer of a conjugated polymer and at least one layer of a low molecular weight compound.

15. An organic light-emitting device according to any of claims 1 to 14, further comprising a substrate, wherein the anode is formed over the substrate and the cathode is formed over the at

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least one layer of organic material.

16. An organic light-emitting device according to any of claims 1 to 14, further comprising a substrate, wherein the cathode is formed over the substrate and the anode is formed over the at least one layer of organic material.

17. An organic light-emitting device according to claim 15 or 16, wherein the substrate comprises one of a glass or a plastics material.

18. An organic light-emitting device according to claim 17, wherein the substrate comprises polyester, polycarbonate, polyimide or poly-ether-imide.

19. An organic light-emitting device according to any of claims 1 to 18, wherein the anode comprises one of indium-tin oxide, tin oxide or zinc oxide.

20. An organic light-emitting device according to any of claims 1 to 19, wherein the first layer of conductive cathode material is sputter deposited.

21. An organic light-emitting device according to any of claims 1 to 19, wherein the first layer of conductive material is evaporated.

22. An organic light-emitting device according to any of claims 1 to 21, wherein the second layer of conductive material is sputter deposited.

23. An organic light-emitting device according to any of claims 1 to 21, wherein the second layer of conductive material is evaporated.

24. A method of fabricating an organic light-emitting device, comprising the steps of:

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forming a cathode for the device over a substrate, which step comprises forming a first layer of a conductive material of high conductivity over a substrate and forming a second layer of a conductive material having a low work function over the first layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV;

forming at least one layer of a light-emissive organic material over the cathode; and

forming an anode for the device over the at least one layer of organic material.

25. A method of fabricating an organic light-emitting device, comprising the steps of:

forming an anode for the device over a substrate;

forming at least one layer of a light-emissive material over the anode; and

forming a cathode for the device over the at least one layer of organic material, which step comprises forming a second layer of a conductive material having a low work function over the at least one layer of organic material and forming a first layer of a conductive material of high conductivity over the second layer of conductive material, wherein the first layer of conductive material is an opaque metallic layer and the second layer of conductive material is substantially thinner than the first layer of conductive material having a thickness of at most 5 nm, and comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.7 eV.

26. A method of fabricating an organic light-emitting device according to claim 24 or 25, wherein the second layer of conductive material has a thickness in the range of from 0.5 to 2 nm.

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27. A method of fabricating an organic light-emitting device according to any one of claims 24 to 26, wherein the second layer of conductive material has a thickness of about 0.5 nm.
28. A method of fabricating an organic light-emitting device according to any one of claims 24 or 27, wherein the substrate comprises one of a glass or a plastics material.
29. A method of fabricating an organic light-emitting device according to claim 28, wherein the substrate comprises polyester, polycarbonate, polyimide or poly-ether-imide.
30. A method of fabricating an organic light-emitting device according to any of claims 26 to 29, wherein the anode comprises one of indium-tin oxide, tin oxide or zinc oxide.
31. A method of fabricating an organic light-emitting device according to any of claims 26 to 30, wherein the first layer of conductive material has a thickness in the range of from 100 to 500 nm.
32. A method of fabricating an organic light-emitting device according to claim 31, wherein the first layer of conductive material has a thickness of about 150 nm.
33. A method of fabricating an organic light-emitting device according to any of claims 26 to 32, wherein the first layer of conductive material comprises Al or an alloy thereof.
34. A method of fabricating an organic light-emitting device according to any of claims 24 to 33, wherein the second layer of conductive material comprises an elemental metal, an alloy or an intermetallic compound having a work function of at most 3.2 eV.
35. A method of fabricating an organic light-emitting device according to any of claims 24 to 34, wherein the second layer of conductive material comprises one of an alkali metal, an alkaline

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earth metal or a lanthanide, or an alloy or an intermetallic compound thereof.

36. A method of fabricating an organic light-emitting device according to claim 35, wherein the second layer of conductive material comprises one of Ca, K, Li, Sm or an Al-Li alloy.

37. A method of fabricating an organic light-emitting device according to any of claims 24 to 36, wherein the ratio of thicknesses of the first layer of conductive material to the second layer of conductive material is at least 20 : 1.

38. A method of fabricating an organic light-emitting device according to any of claims 24 to 37, wherein the at least one layer of organic material has a thickness of about 100 nm.

39. A method of fabricating an organic light-emitting device according to any of claims 24 to 38, wherein the organic material is a conjugated polymer.

40. A method of fabricating an organic light-emitting device according to any of claims 24 to 38, wherein the organic material is a low molecular weight compound.

41. A method of fabricating an organic light-emitting device according to any of claims 24 to 38, wherein the at least one layer of organic material comprises a composite structure including at least one layer of a conjugated polymer and at least one layer of a low molecular weight compound.

42. A method of fabricating an organic light-emitting device according to any of claims 24 to 41, wherein the first layer of conductive material is sputter deposited, preferably by DC magnetron or RF sputtering.

43. A method of fabricating an organic light-emitting device according to any of claims 24 to 41, wherein the first layer of

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conductive material is evaporated, preferably by resistive or electron-beam thermal evaporation.

44. A method of fabricating an organic light-emitting device according to any of claims 24 to 43, wherein the second layer of conductive material is sputter deposited, preferably by DC magnetron or RF sputtering.

45. A method of fabricating an organic light-emitting device according to any of claims 24 to 43, wherein the second layer of conductive material is sputtered, preferably by DC magnetron or RF sputtering.

46. An organic light-emitting device, comprising at least one layer of a light-emissive organic material arranged between an anode and a cathode for the device, wherein the cathode comprises a first layer of a conductive material which is a DC magnetron sputtered metallic layer of high conductivity and a second layer of a conductive material having a low work function arranged between the at least one layer of organic material and the first layer of conductive material, wherein the second layer of conductive material is substantially thinner than the first layer of conductive material.

47. An organic light-emitting device substantially as hereinbefore described with reference to the accompanying drawings.

48. A method of fabricating an organic light-emitting device substantially as hereinbefore described with reference to the accompanying drawings.

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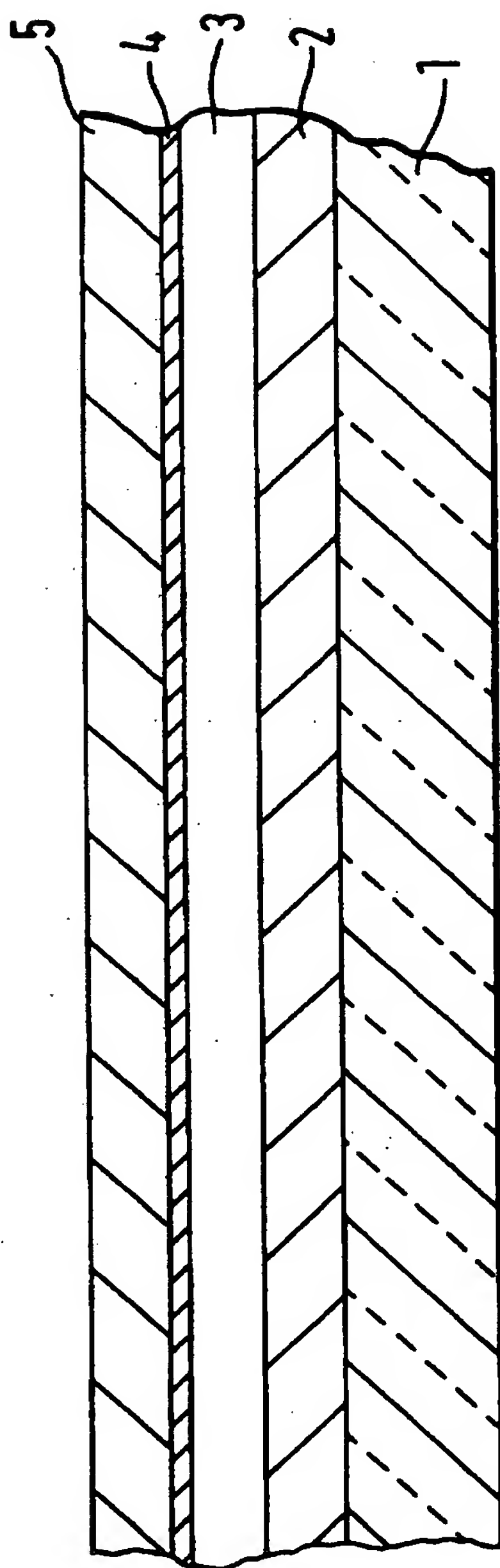


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inter. Application No.

PC1/GB 97/02380

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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